

Supporting Information

Achieving Mechano-Upconversion-Downshifting-Afterglow Multimodal Luminescence in Pr³⁺/Er³⁺ Coactivated Ba₂Ga₂GeO₇ for Multidimensional Anticounterfeiting

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1. Experimental Section

1.1 Preparation of Multimodal Material: samples of $\text{Ba}_{2-x-y}\text{Ga}_2\text{GeO}_7:x\text{Pr}^{3+}, y\text{Er}^{3+}$ ($x=0.04, y=0.08$) were synthesized through conventional high temperature solid-state method. BaCO_3 (99.99%), Ga_2O_3 (99.99%), GeO_2 (99.99%), Pr_6O_{11} (99.99%) and Er_2O_3 (99.99%) were used as raw materials, and were weighed in atomic ratio of Ba, Ga, Ge, O, Pr and Er in chemical formula $\text{Ba}_{1.88}\text{Ga}_2\text{GeO}_7: 0.04 \text{Pr}^{3+}, 0.08\text{Er}^{3+}$ (Abbreviated as BGGO: $\text{Pr}^{3+}, \text{Er}^{3+}$). Afterwards, the above materials were mixed homogeneously in agate mortar with ethanol. The pre-sintered mixture was transferred into muffle furnace and sintered at 10h in atmosphere. After cooling naturally room temperature, the obtained sample was grinded powder in agate mortar for further test.

1.2 Fabrication of ML elastomer: Polydimethylsiloxane (PDMS, Sylgard184, Dow Corning) were used to assemble the ML elastomer film for BGGO: $\text{Pr}^{3+}, \text{Er}^{3+}$. First, 1.5 g PDMS, 0.8 g BGGO: $\text{Pr}^{3+}, \text{Er}^{3+}$ powder and 0.3 g curing agent were finely mixed in a petri dish with a diameter of 60mm. Then, the mixture was laid tidily in circular iron model with shallow groove. After curing at 60°C for 1day. The PDMS-BGGO: $\text{Pr}^{3+}, \text{Er}^{3+}$ ML elastomer was prepared.

1.3 Fabrication of the multimodal anticounterfeiting device: The mixed BGGO: $\text{Pr}^{3+}, \text{Er}^{3+}$ / PDMS slurry was printed as a leaf by 3D printing technique. Subsequently, the leaf was dried at 60 °C for 4h. Moreover, the BGGO: $\text{Pr}^{3+}, \text{Er}^{3+}$ / PDMS elastomer was cut into strips, which represents various encryption information. The strips were coated with pure PDMS and cured at 60 °C for 4 h. Finally, the multimodal anticounterfeiting device and the cured elastomer with ML patterns was fabricated.

2 Characterizations

The X-ray diffraction (XRD) patterns of LCAO and Ln doped LCAO were collected on a Rigaku D/Max-2400 X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) at 2θ range from 10° to 90° . The Rietveld XRD refinement of undoped and doped LCAO were performed by the general structure analysis system (GSAS) software. The PL, PL excitation (PLE), PersL and UC spectra were recorded on FLS-920T fluorescence spectrophotometer equipped with Xe lamp, 980 and 808 nm laser. The ML spectra of PDMS- BGGO: $\text{Pr}^{3+}, \text{Er}^{3+}$ elastomers were in situ recorded with a home-made uniaxial tensile testing machine to a fluorescence spectrophotometer equipped with a CCD camera (IVAC-316) at a frame rate of 50 fps. The PersL decay curves of BGGO: $\text{Pr}^{3+}, \text{Er}^{3+}$ powders were measured by an LMT-Photometer B 520L. The diffuse reflectance (DR) spectra were performed using a Perkin Elmer LAMBDA 950. The thermoluminescence (TL) curves were measured on a TL dosimeter (Beijing Nuclear Instrument Factory) in a temperature range between 298.5 K and 673.5 K with a 1 K s^{-1} calefaction rate. The energy dispersive spectra (EDS) and mapping were recorded by a field-emission (FEI) TecnaiF30 transmission electron microscope. The valence states of Pr and Er were identified by an X-ray photoelectron spectrometer (XPS) (PHI-5702 instrument).

3 Computational methods

All electronic structure calculations are performed by the CASTEP code. In our electronic structure calculations, all ion-electron interactions employ the ultra-soft pseudopotential introduced by Vanderbilt. The effects of exchange–correlation interaction is treated within the generalized gradient approximation (GGA) proposed by Perdew et al. In our calculations, we use $U = 4.5 \text{ eV}$ for Fe atom. The self-consistent convergence of the total energy is $2.0 \times 10^{-6} \text{ eV/Atom}$, the maximum ionic Hellmann–Feynman force is 0.03 eV/\AA , the maximum ionic displacement is $2.0 \times 10^{-3} \text{ \AA}$, and the maximum stress is 0.02 GPa. These parameters are carefully tested and sufficient to lead to a well-converged total energy.

4 Supporting Picture

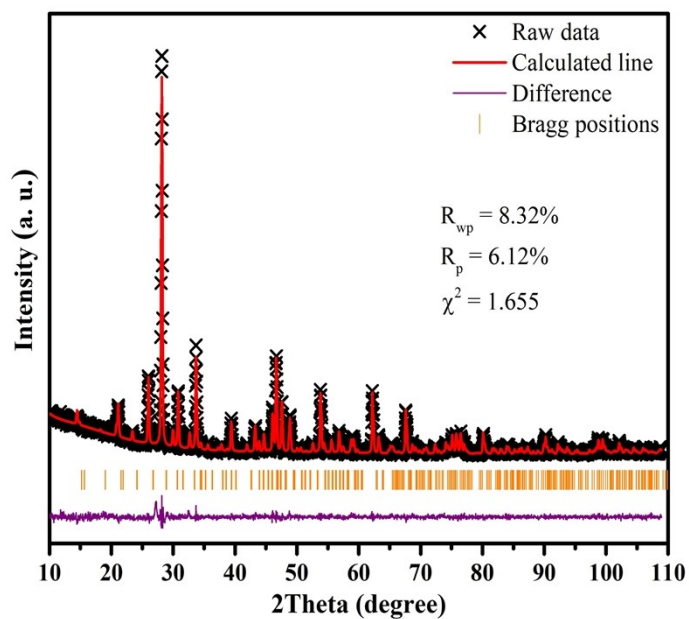


Figure S1 The Rietveld refinement of BGGO host.

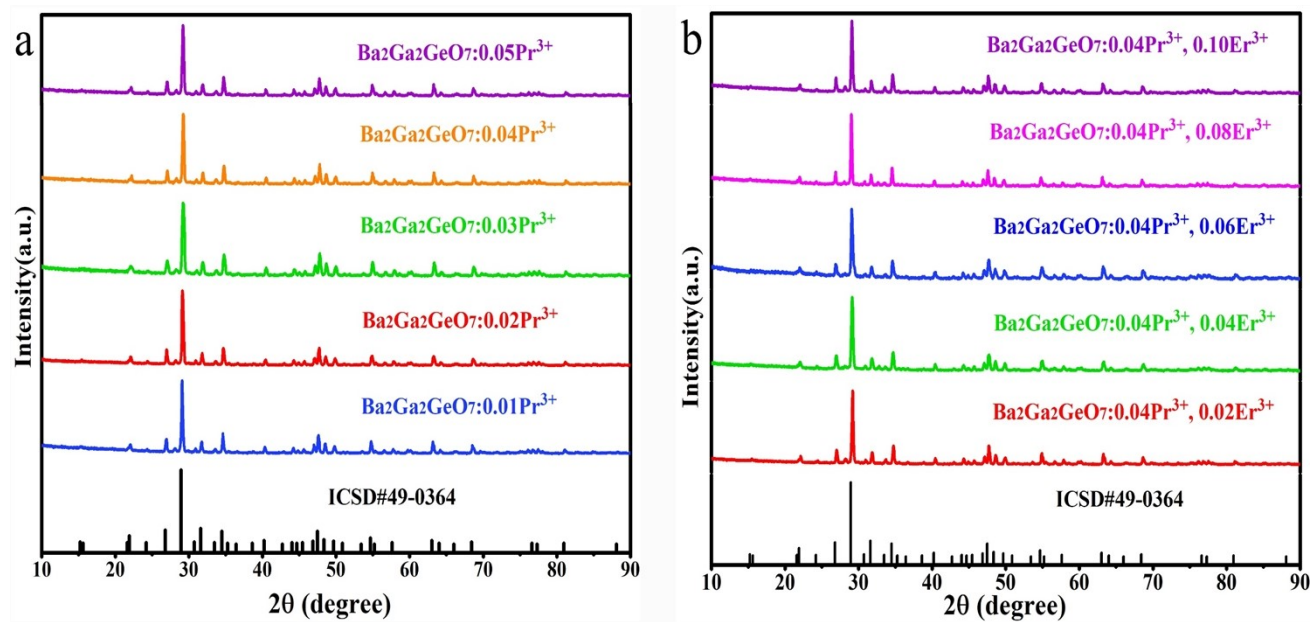


Figure S2 (a-b) XRD pattern of BGGO: xPr³⁺ and BGGO: 0.04Pr³⁺, xEr³⁺ phosphor, respectively.

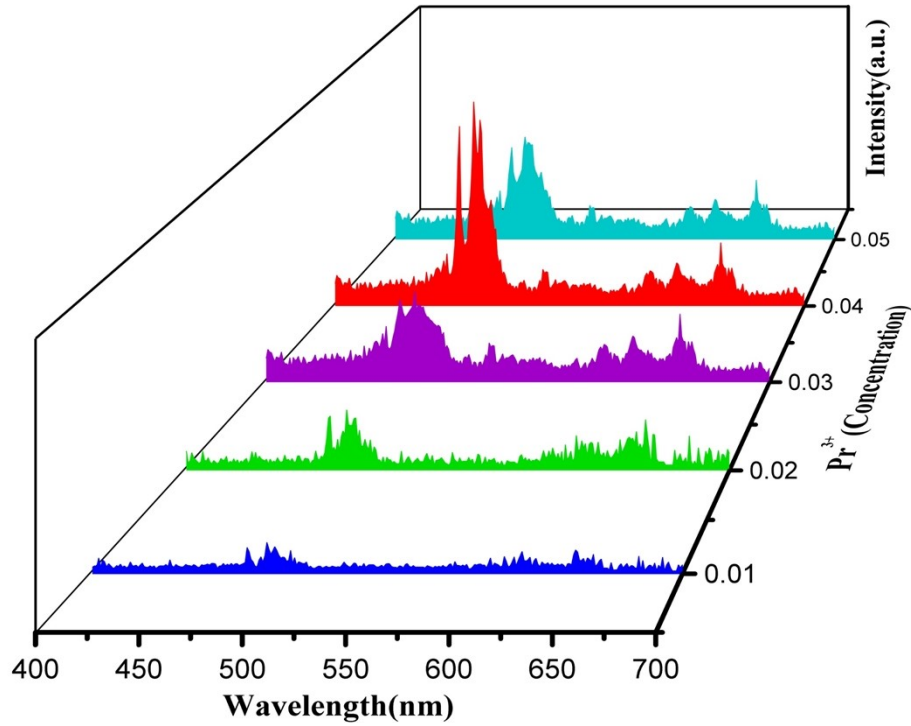


Figure S3 The PL spectra of $\text{Ba}_{2-x}\text{Ga}_2\text{GeO}_7: x\text{Pr}^{2+}$ ($0.01 \leq x \leq 0.05$) under the 254nm UV light excitation. The optimal concentration is 0.04mol, beyond which the PL intensity decreases significantly.

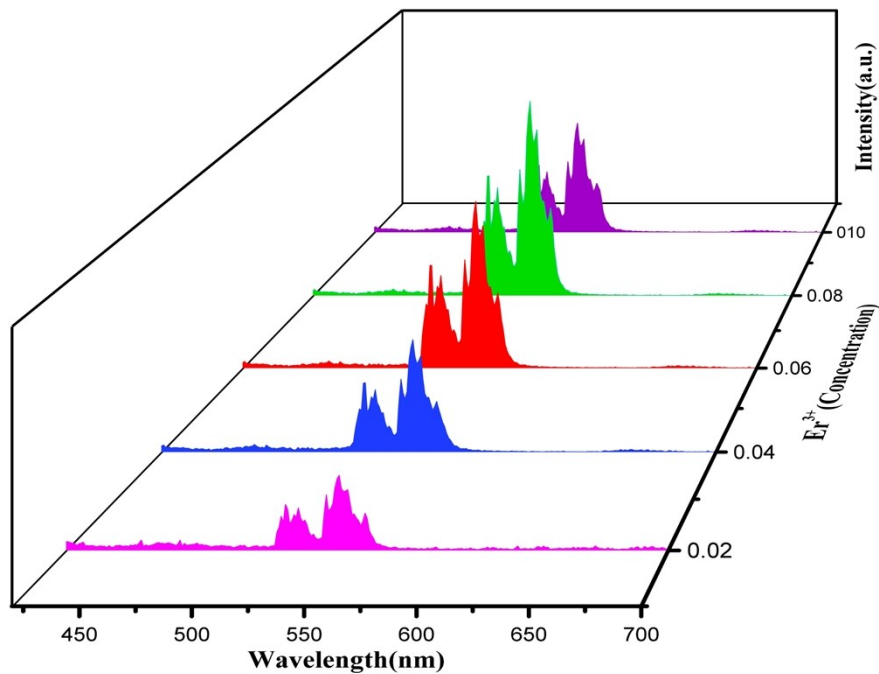


Figure S4 The PL spectra of $\text{Ba}_{2-x}\text{Ga}_2\text{GeO}_7: x\text{Er}^{3+}$ ($0.02 \leq x \leq 0.10$) under the 379nm UV light excitation. The optimal concentration is 0.08mol, beyond which the PL intensity decreases significantly.

Elements	Atomic number	Normalized mass (%)	Atomic (%)	Abs. error (%)
Ba	56	16.15	12.58	1.17
Ga	31	13.33	13.71	0.7
Ge	32	7.66	7.48	0.42
O	8	2.00	8.85	1.45
Pr	59	2.30	2.64	0.31
Er	68	5.2	2.16	0.36
Cu	29	51.61	55.58	2.53

Table S1 the atom ratio and weight of BGGO: Pr³⁺, Er³⁺ phosphor based on EDS.

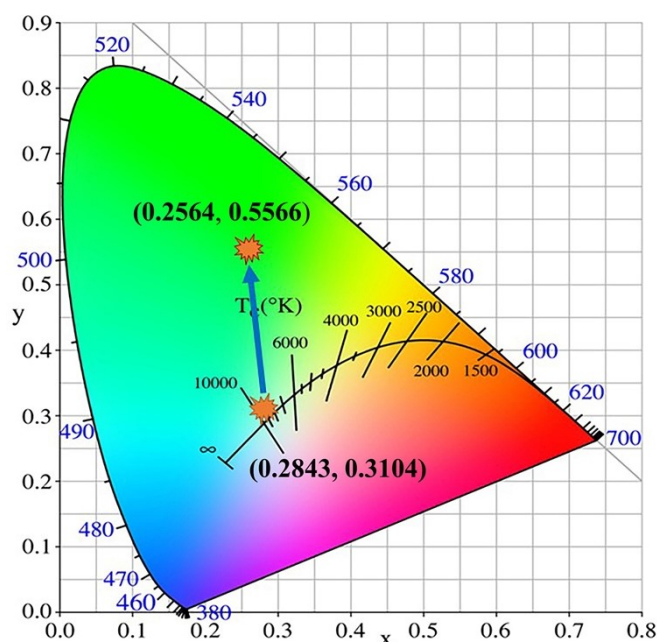


Figure S5 the CIE chromaticity coordinate positions of BGGO: Pr³⁺, Er³⁺ sample under the 254nm and 379nm irradiation, respectively.

Figure S5 displays the CIE chromaticity coordinate positions of BGGO: Pr³⁺, Er³⁺ sample under the 254nm and 379nm irradiation, respectively, it's obviously observed that the CIE chromaticity coordinate changes with the excitation wavelength and the corresponding colors tuned from white to green.

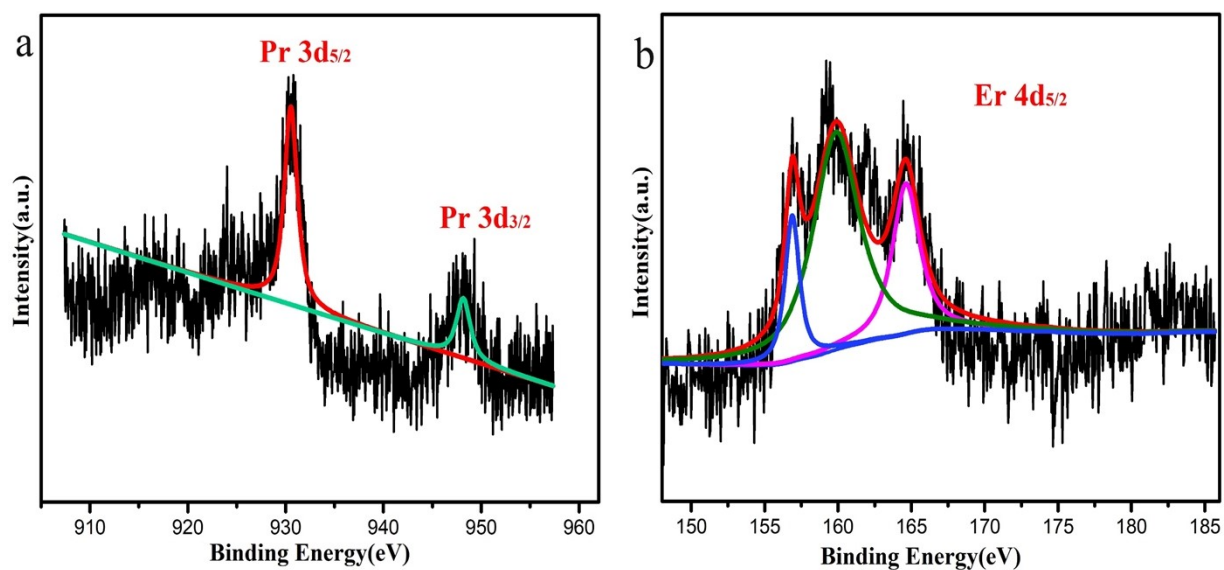


Figure S6 The high-resolution XPS spectra of Pr (3d_{5/2}, 3d_{3/2}) and Er 4d_{5/2}.

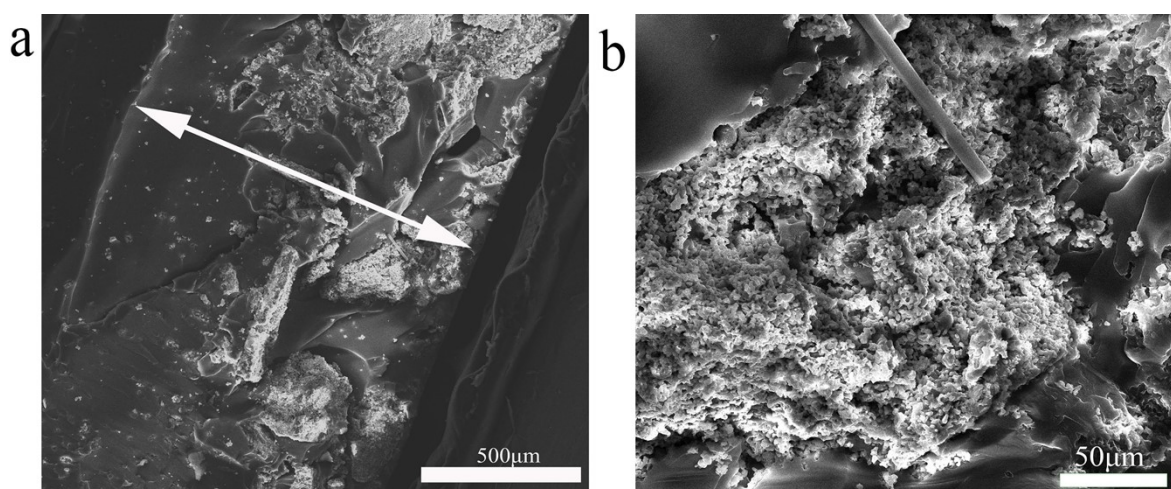


Figure S7 (a) the cross-sectional SEM photograph of LCAO: Eu^{2+/3+}, Yb³⁺, Er³⁺ /PDMS composite elastomer;(b) the morphology of the LCAO: Eu^{2+/3+}, Yb³⁺, Er³⁺ /PDMS composite elastomer (thickness of ca. 1 mm).